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On the chemistry of petroleum and coal

Hans-Henning OELERT and Lado LENART

Petroleum and coal are determining factors of our present life style in many respects. At present they still are the mainstay of energy production, energy transformation (electrification) and also of domestic heat generation (light fuel oil and domestic coal). In addition to serving as a source of energy, coal today is actually used only in chemically upgraded form in metallurgy and in the near future will be utilized to an increasing degree for producing gas. In the highly traditional field of chemistry, coal as raw material has largely been replaced by petroleum. More than 80% of the key chemicals of organic chemistry and chemical engineering are derived from petroleum. Starting from crude oil and natural gas, petrochemistry supplies feedstocks for a variety of chemical engineering processes. We can therefore say without exaggerating that at present life as we know it today would be unimaginable without petroleum.

In the following we will attempt to elucidate the chemical composition of petroleum and coal, to outline various procedures of primary processing in their present form, and to demonstrate future aspects of a more intensive chemical utilization and its technological problems.

Composition

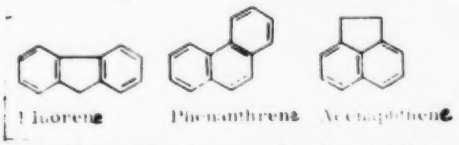
Petroleum and coal are natural multicomponent mixtures of organic substances. Their composition can first be regarded globally in terms of molecular size and molecular structure. Molecular size, expressed as molecular weight, ranges from 16 (methane) to about 10^4 (petroleum) and 10^6 (coal). These, however, are merely limiting values which still do not tell us anything about the distribution of the molecules within the stated range. Molecular structure can be seen in terms of different types of structure. In principle, each type of molecular structure within the above range is characterized by the arrangement of the carbon framework. Paraffins with straight carbon chains (n-paraffins), paraffins with branched carbon chains (iso-paraffins), cycloalkanes, and aromatics are the basic types; each of these types may at the same time act as a substituent in any of the other types. An aromatic type of structure like naphthalene, for example, may be linked directly to an alicyclic ring by two bonds, and the ring system thus expanded may contain paraffinic substituents. The resultant structure is called an alkyl-substituted naphthenic aromatic. The olefins not listed among the structures above play virtually no part among natural raw materials. Much more important are the heteroatoms, predominantly sulphur, oxygen, nitrogen and traces of some metals, which have been incorporated in the organic molecular structures and generally are called hetero fractions.

Any of these types may of course occur in different molecular sizes. Thus the global distribution of molecular sizes is composed additively of the distributions into the various types of structure. It is the aim of analysis in synthetic organic chemistry and numerous other fields to isolate and identify individual chemical substances. In the case of such widely occurring multi-

component mixtures as petroleum and coal, however, this can be done only for fairly small molecules within limits that are accessible to modern separating techniques, above all gas chromatography. Our present substantiated knowledge of various constituents of coal and petroleum has been briefly summarized below.

Bituminous coals

In view of the chemical and physical properties involved, our knowledge of defined substances in coal is limited. Medium-rank and above all low-rank bituminous coals contain 1-2% n-paraffins belonging to the wax fraction. The major share presumably have chain lengths of 12 to more than 35 carbon atoms. Smaller aromatic molecules such as naphthalene, methyl-, dimethyl- and trimethyl naphthalenes, fluorene, phenanthrene, anthracene

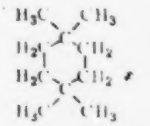


have been identified directly in coals in orders of magnitude of 0.1 - 0.5 per mille by analyses under mild conditions (stripping off at 400°C). In extracts, the yields of which are low, substituted benzenes and naphthalenes are the major constituents. Acenaphthenes and phenanthrenes play a secondary role, and other types of aromatics occur only in insignificant quantities. Very few and usually insufficient data on individual hydrocarbons are available for larger molecules. In the case of hetero compounds the only individual substances so far identified are small molecules.

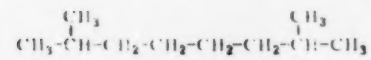
Some data exist on phenols. In global terms, oxygen is exocyclic (presumably also in larger molecules), as in phenols,

sulphur partly exocyclic, partly endocyclic (as in thiophenes), and nitrogen endocyclic (as in pyridine).

Our knowledge of coals is limited mainly because major methods of instrumental analysis today are not very well suited for mixtures of solids such as coals. However, infrared spectroscopy at least gives an approximate idea of the chemical structure of coal. It can be used to determine the structural groups that statistically make up coal. By structural groups we mean not only functional groups such as methyl or hydroxyl groups but also structural elements such as quaternary carbon atoms. The sum total of all structural groups makes up the molecule, although this should be taken only in a statistical sense. A simple example to illustrate this: Infrared spectroscopy sees 1,1,4,4-tetramethylcyclohexane and 2,7-dimethyloctane as identical. The molecules of both substances, statistically speaking, consist of four methyl groups, four methylene groups, and two tertiary or quaternary carbon atoms, respectively. It would therefore be impossible to



1,1,4,4-Tetramethylcyclohexane



2,7-Dimethyloctane

evaluate a mixture of these two substances as to type or quantity of its components. Such spectral data are relatively useless for a mixture of smaller molecules as e.g. gasoline, for gas chromatography alone gives a much more differentiated and accurate picture. For coal as a mixture of solids, however, they are at present among the most accurate information obtainable.

Figure 1 is a plot of the distribution of carbon in coals into different bond types over the technologically important parameter of volatiles content (weight loss at high temperatures under defined conditions). Increasing volatiles contents in first approximation run parallel to decreasing carbon contents. With maximum levels of 7-8%, carbon attached to hydroxyl groups and in methyl groups is merely a secondary constituent. Carbon in methylene groups and also carbon in aromatic CH groups does not occur in appreciable amounts until coals with more than 10% volatiles. The aromatic CH group content passes through a broad maximum, but in coals with more than 20% volatiles already decreases again from that level. By contrast, the concentration of CH_2 groups, most of which are part of naphthene rings, after a constant range increases in coals with higher volatiles contents. This tendency to opposite directions in more volatile and therefore lower-rank coals can be explained mainly by dehydrogenation-hydrogenation reactions in the course of coal formation. Especially the distinct conversion at about 28% volatiles, generally called coalification step, has a direct bearing also on the technological properties of coal (compression strength, grindability, thermal decomposition, degasification). Statistically, the dominant role clearly is played by aromatic carbon which is no longer attached directly to hydrogen (C_{ar}). Above it was already assigned to the bond types of substitution and ring linkage. Even if all methylene and methyl groups occur in substituents, at volatiles contents below 28%, about 40% of total carbon would still have to occur in ring form. This, however, could be explained only by either very large aromatic systems condensed throughout or linking CC bonds between medium-sized ring systems. Ultimately, both versions result in a polymeric system. Other analytical data and particularly the physical behaviour of coals are more in favour of the second version.

One essential parameter, however, namely mean molecular weight, cannot be measured for coals with this method. Values between 300 and 600 are obtained for coal products such as those from lignite liquefaction, but much higher values have to apply to coal, a mixture of solids. Certain chemical manipulations have to be tolerated to estimate the molecular weight of different coals: After chemical reactions such as alkylation or acylation, a major part of coals (85%) can be dissolved. Molecular weights can then be determined directly from these soluble products. As Figure 2 based on mining studies in Essen shows, extractability but proportionally to it also molecular weight increase with increasing chemical manipulation. The relationship here is clearly determined by the nature of the parent coal. It should also be mentioned that we have here products of a chemical reaction in which presumably bonds are cleaved; the molecular weights or, to use a more cautious expression, the particle weights in the original coals may be considerably higher. Without chemical manipulation, a maximum of about 20% of the coal can be dissolved. Gel chromatographic studies on the molecular size distribution of such extracts show that at molecular weights up to a few hundred, in addition to a still individually structured range the major portion occurs in the range of above 500 to approx. 3000. Relatively little substance seems to occur in the range from 3000 to 10,000. Experiments carried out at the Max Planck Institute of Coal Research show clearly that the true or apparent molecular weights of a considerable, if not the major, portion of coals range up to about 10^6. However, this range is not yet accessible with present separating techniques.

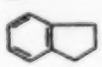
Tars and pitches

We know more about constituents in pyrolytic products of coals. A large body of extensive, generally known data exists which is the result of research work in the last 50 years or so. We cannot deal with these data in detail here, but would like to characterize the nature of those findings by two points. Aromatic structures whose degree of condensation increases with molecular weight clearly dominate. The number and size of aliphatic substituents are small. For all these data it must be carefully established to what extent the structures in question were already present in the parent coal or are the result of thermal reactions.

Petroleum hydrocarbons

On account of the better separation and detection methods available for petroleum we have more extensive data on this material. Information is particularly comprehensive for the fraction with boiling temperatures up to about 200°C. Figure 3 represents the distribution curves of the four major types of compounds for mean values of a representative selection of crude oils. Paraffins dominate greatly, and they are characterized by the fact that even-numbered components usually are most frequent. The situation is similar for (substituted) cyclopentanes and cyclohexanes. Monoaromatics have shifted into the region of larger molecules with numerous carbon atoms. We still have a wealth of individual data for the boiling range of 200-300°C, but no comprehensive picture on account of the greatly increasing number of isomers and of the insufficient accuracy of separating techniques. In this range, too, n- and iso-paraffins are most frequent, and among them

the isoprenoids* merit special attention. There are both monocycloalkanes and bicycloalkanes. The aromatics are represented by polysubstituted benzenes, very many usually polysubstituted naphthalenes, also indanes, tetralins, diphenyls, acenaphthenes, and fluorenes. To the extent quantitative analysis has been possible, the quantitative proportions of individual components are very small. So far it has been possible only in few cases to isolate and identify higher hydrocarbons in the boiling range above 300°C.


Indane

Tetralin

Higher n-paraffins, isoprenoids (terpenes and triterpenes) and hydrocarbon derivatives of the sterols**, as well as a few, always polysubstituted condensed aromatics have been identified. It is not possible to obtain a complete picture. The only clues to the composition of the highest boiling and non-boiling ranges come from collective type or class analyses.

Hetero compounds in petroleum

Extensive data are available also on hetero compounds, but

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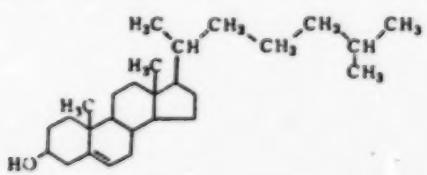
* Isoprenoids are hydrocarbons consisting of isoprene units. To them belong numerous natural substances, e.g. the terpenes which are made up of two, three (sesquiterpenes), four (diterpenes), six (triterpenes) or eight (tetraterpenes) isoprene units.

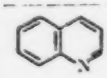
** Sterols are secondary alcohols with a characteristic tetracyclic ring system consisting of three six-membered carbon rings and one five-membered one. The most common representative of this group is cholesterol.



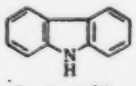
Cholesterol

none of them permit quantitative evaluation; they also become steadily scarcer with increasing molecular size. In the low-boiling range, sulphur-containing compounds occur as mercaptanes, sulphides and thiophenes; in higher-boiling ranges, benzo- and dibenzothiophenes and even more highly condensed thiophenes were found to be the major constituents. Even in the highest-boiling fraction sulphur appears to be predominantly heterocyclic. Type and concentration of individual sulphur compounds vary greatly among various crude oils.

Nitrogen is almost always heterocyclic, occurring in usually substituted pyridines, quinolines, and carbazoles. Nitrogen contents frequently rise noticeably with boiling point. In the highest-boiling fractions nitrogen and oxygen frequently occur in one and the same molecule. Data on oxygen-containing constituents



Quinoline



Carbazole

are scarce. Obviously, on the whole carboxyl compounds are the most common substances. Especially in the last few years several isoprenoid acids and many naphthenic acids*, deriving mainly from sterols, have been detected.

The work done by W.K. SEIFERT on naphthenic acids exemplifies the progress made in recent years in isolating and identifying individual substances. Several of these compounds were detected in a Californian crude oil more than 10 million years old by multi-stage separation and combined gas chromatography/high-resolution mass spectrometry. In crude oil, for instance, a C_{24} naphthenic acid was detected which very probably was formed by

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* In petrochemistry, cyclic alkanes are known as naphthenes. Napththenic acids therefore are alicyclic carboxylic acids.

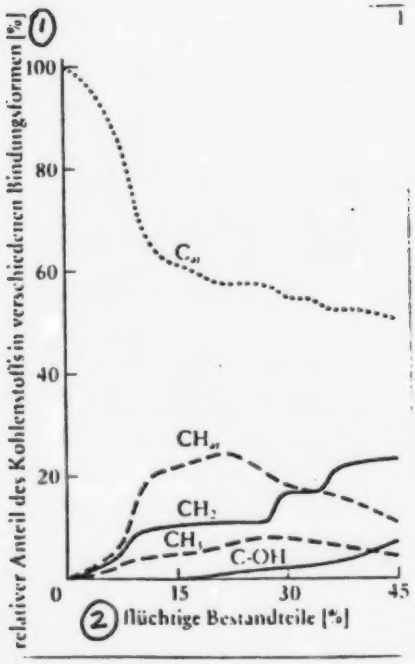


Figure 1. Distribution of carbon in various coals into different bond types. Abscissa: volatiles in percent. A coal with 15% volatiles for instance has a total carbon content of approx. 91%; a coal with 30% volatiles has a carbon content of approx. 87%, one with 45% volatiles, a carbon content of approx. 75%.

Key: 1 - relative carbon concentrations in various bond types, %
2 - volatiles, %

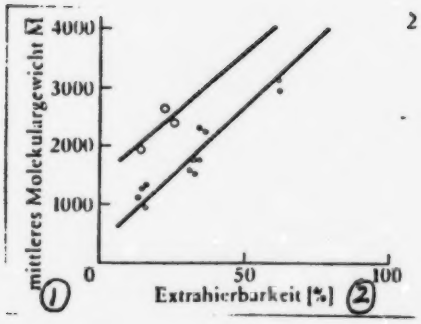


Figure 2. Solubles of two different coals (shown on abscissa as extractability) as a function of mean molecular weight M. Extractability and mean molecular weight clearly are approximately proportional to each other, with the slope of the straight line depending on the type of coal.
Red curve* = coal with 24% volatiles
Black curve* = coal with 19% volatiles

Key: 1 - mean molecular weight M
2 - extractability, %

* Translator's note: The photocopy submitted for translation does not distinguish between red and black.

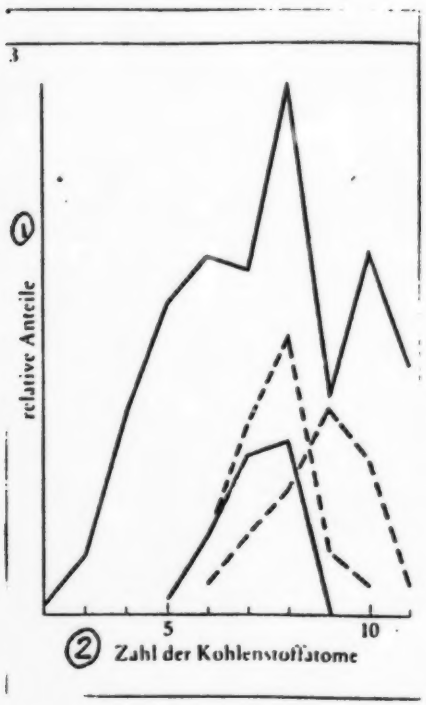
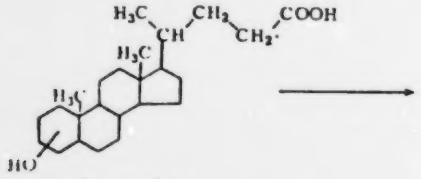


Figure 3. Distribution of four types of compounds in a representative selection of oils (mean values).
Red solid curve* = paraffins
Black solid curve* = cyclopentanes
Red dashed curve* = cyclohexanes
Black dashed curve* = monoaromatics

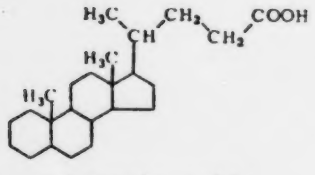
Key: 1 - relative concentrations
2 - number of carbon atoms

* Please see Translator's note on p. 11.

dehydrogenation and subsequent hydrogenation of a C_{24} bile acid such as it occurs in amphibians and various lower animal species. This structure which proves that (presumably a very small) part of petroleum originates from animal material obviously has remained relatively unchanged throughout the manifold and lengthy processes of petroleum formation.



C_{24}-bile acid



C_{24}-naphtnenic acid

Molecular weight distribution in petroleum

We have seen that in coals considerable chemical manipulation is needed to determine the mean molecular weight from the fractions that have become soluble by that manipulation. In petroleum, in view of its virtually complete solubility, such determination is no problem, and gel permeation chromatography even permits plotting molecular weight distribution curves. Figure 4 shows such distributions for six German crude oils determined by means of preparative chromatography. It is a plot of weight percentages of substance in 1 mL eluate over the molecular weights

determined for individual fractions. The fraction ranging from gasoline to lubricating oil - up to molecular weights of 600 - does not dominate in all crude oils. The Gernsheim crude is the one closest to this assumption. By contrast, the bitumen fractions with high molecular weights dominate in other crudes. This is most obvious in the case of the Meppen crude where the largest fraction is that with molecular weights of 400 to approx. 1000, although even the fractions with still higher molecular weights are considerable. In particular the higher-molecular fractions in crude oils do not consist only of hydrocarbons but mostly contain also large fractions of hetero compounds. The basic and acid compounds can be separated out fairly easily on suitable ion exchangers and can again be examined for distribution of molecular weights.

Figure 5 shows the distribution curves of the hydrocarbon, basic, and acid fractions in the vacuum distillate of a crude oil. Except for a low-molecular shoulder the hydrocarbon fraction has a relatively continuous, almost symmetrical distribution. The distribution of the nitrogen-containing basic fraction is similar but shifted towards higher molecular weights by a certain amount; it has a secondary maximum at considerably higher molecular weights. The distribution of the acid fraction follows a completely different course. Most of it appears at formally much higher molecular weights, but it has been shown that mostly these are dimers of constituents which as monomers fall within the ranges of the two other fractions. Gel chromatographic data on molecular weight distributions in crude oils reveal that the main fraction lies in the molecular weight range of 200 - 800. At weights above 1000 the distribution curves drop sharply. The highest particle weights determined experimentally in petroleum asphalthenes range up to 4000; these presumably are already association products. More

recent studies by means of ultrafiltration and ultracentrifugation make particle weights of up to 1,000,000 seem possible. However, we as yet know very little about these ranges.

Even at medium molecular weights the number of isomers within the various types of compounds is so great that none of the modern separation techniques can succeed in isolating and identifying all individual substances. At present therefore we can merely try and separate individual substances from each other as accurately as possible and analyze the resultant concentrates further, again more in statistical terms.

Industrial processing

The manner of chemical and physical processing of petroleum and coal depends on molecular weight distribution rather than on chemical structure. Thus petroleum, being a mixture of liquids, can first be separated by physical methods and then the various fractions can be transformed chemically. Coal cannot be handled this way. It must first be transformed by chemical reactions - pyrolysis, hydrogenation or gasification - into an intermediate product which then can be further broken down or transformed chemically.

Breakdown of petroleum

The physical separation technique most frequently employed to break down crude oil is fractionating distillation at standard pressures; vacuum distillation columns can be used where higher separation efficiencies are required. The distillates cover the wide range from gas fraction to bituminous residues. The gas fraction contains hydrogen and hydrocarbons as far as ethane, also certain quantities of C_3 and C_4 hydrocarbons. The main constituents of the next fraction, the so-called liquid gas, are butane

and propane. The gasoline fraction with boiling points up to 180°C contains paraffins as far as isooctane, olefins as far as trimethyl-2-pentene, aromatics (benzene, toluene, ortho-, meta-, para-xylenes, etc. as far as isopropylbenzene), and naphthenes (cyclopentane to propylcyclohexane). Kerosene, the next distillate fraction, boils in the range of 180-230°C; characteristic of this fraction are its higher bicycloparaffin and binuclear aromatic contents. The next fractions are the middle distillates with boiling points of 230-305°C, containing higher-molecular hydrocarbons, e.g. C_{13} to C_{17} n-paraffins. The higher-boiling distillates are known commercially as diesel fuel, light fuel oil, heavy fuel oil, vacuum distillate (lubricating oils as far as cylinder oil), and vacuum residues. As regards chemical structure, these distillates are increasingly more complex multicomponent mixtures of increasing molecular weights.

Conversion of petroleum fractions

For economic reasons, some higher-boiling fractions are converted into low-boiling substances by pyrolysis or catalysis. Suitable methods are thermal and catalytic cracking, mainly with heavy petroleum distillates and distillation residues as feedstocks. During thermal cracking at temperatures of 425-500°C, C—C bonds in the larger paraffin molecules are cleaved and unsaturated hydrocarbons are formed; the main products of this process are gases and liquids in the gasoline range. Catalytic cracking is similar to thermal cracking, but it has the advantage that certain reactions take place at an accelerated rate; for instance higher yields of C_3 and C_4 hydrocarbons with considerable unsaturated hydrocarbon contents are obtained which can be alkylated and used as petrochemical feedstock.

Hydrocracking corresponds to catalytic cracking augmented by hydrogenation. This process is highly flexible with regard to feedstocks and resultant products. Olefins are hydrogenated, gasoline becomes stable. There are single-stage and two-stage techniques; temperatures used are 300-470°C, pressures 70-180 at.

A process technologically related to thermal cracking is thermal reforming; it employs temperatures of 525-575°C and pressures of 25-45 at. The basic difference compared to cracking is the fact that the aim is not cleaving of large molecules but producing knock-free gasolines by isomerization and aromatization. The reformate also contains considerable quantities of olefins, since cleaving reactions can never be completely prevented. Another method of producing gasoline fractions is catalytic reforming. It is based on paraffins cyclizing to cycloalkanes and subsequent dehydrogenation with precious metal catalysts to form aromatics.

Thermal reformates and to a certain extent also catalytic reformates are unstable on account of the extensive cleavage of hydrogen. A suitable stabilizing measure is hydrogenation under pressure. The fuels in the gasoline range, instead of the above-mentioned techniques, can also be produced by polymerization, alkylation, and isomerization. Polymerization here means the formation of gasoline hydrocarbons from the C_3 and C_4 olefins present in the cracking gases. In alkylation, straight-chain or branched alkyl groups are added onto other, mostly aromatic systems. One of the most frequent feedstocks for this process is isobutane which is produced by isomerization of n-butane.

The above-described methods constitute the basis of fuel and lubricating oil production but also generate petrochemical feedstocks.

Petrochemistry

It is characteristic of the petrochemical industry that the first products of petroleum, a complex multicomponent mixture, are simple low-molecular unsaturated compounds from which the other primary and secondary raw materials of the chemical industry are then synthesized. The major products of the first stages of petrochemistry are acetylene, propylene, isobutene, butadiene, isoprene, and the aromatic primary chemicals benzene, toluene, ortho- and para-xylenes, naphthalene, cyclohexane, etc.

Acetylene is produced by the pyrolysis of light hydrocarbon fractions. Very high temperatures (e.g. light arc technique) are characteristic of acetylene production; by-products are carbon monoxide, hydrogen, and ethylene. Ethylene, today the most important raw material, is produced by thermolysis of saturated hydrocarbons (ethane, liquid gas, light gasolene, heavy crude oil fraction, and crude oil itself). The most common feedstock is light gasoline with a boiling range of 30-180°C. Suitable equipment for ethylene production are pipe furnaces (cleavage temperatures around 800°C, presence of steam or hydrogen) and fluidized bed reactors.

Propylene is obtained as a by-product of ethylene, with catalytic cracking giving particularly high yields.

Isobutene is produced primarily from the C_4 fraction of light gasoline pyrolysis, that fraction containing about 25% isobutene.

Butadiene, the most important unsaturated C_4 hydrocarbon, is produced either by extraction of the C_4 fraction of light gasoline pyrolysis or dehydrogenation of butane by various techniques.

Benzene for synthetic purposes is used mainly for producing cyclohexane, styrene, and phenol. Petrochemical gasoline competes with benzene produced from coke oven gas.

Pure aromatics can be obtained by catalytic reforming of gasoline fractions and subsequent aromatic extraction and fractionation. In addition to the isolation of aromatics from high-aromatic feedstocks, the conversion of excess aromatics plays a major role in aromatic production. The major technical procedures for the separation of aromatics from paraffins and naphthalenes are superfractionation, azeotropic distillation, extractive distillation, and liquid/liquid extraction, occasionally also crystallization. Among conversion techniques we should mention isomerization, either hydrocatalytically or under cracking conditions. A special case is for instance the conversion of isomeric xylenes into each other in accordance with thermodynamic equilibrium conditions. Another technique for aromatic production is dealkylation, where side chains, occasionally also saturated rings, are cleaved from higher aromatic hydrocarbons in the presence of hydrogen either thermally or catalytically. A representative example of this procedure is the production of benzene from toluene and of naphthalene from methyl- and dimethylnaphthalenes; here the feedstocks are various fractions from crude oil processing.

Thermal production of coal chemicals

While in the petroleum industry, petrochemistry in the stricter sense of the term has about the same economic importance as fuel and lubricating oil production, coal chemistry as such today has lost much of its importance. Essentially, it uses standard coal upgrading techniques, i.e. coking at low, medium or high temperatures; that is to say, the volatile pyrolytic products of these techniques are processed. Coal pyrolysis itself takes the following course: Up to 400°C, hydroxyl, methoxyl, and carboxyl groups are cleaved from the coal. This generates small quantities

of steam, carbon monoxide and carbon dioxide; due to the removal of aliphatic groups, the coal becomes somewhat enriched in aromatics. The temperature interval of 400-600°C is the range of softening, main degasification, and semicoke formation, due to cleavage of the bridges between larger alicyclic-aromatic systems. Above 650°C coking takes place, characterized chemically by the cleavage of hydrogen from aromatic structures. Of coal chemical technologies we need to deal here only with the processing of high-temperature coking products since the problems of the other techniques are very similar. The primary, volatile product of coking is crude gas which contains mainly the following: hydrogen, methane, unsaturated hydrocarbons, carbon monoxide, carbon dioxide, nitrogen, ammonia, hydrogen sulphide, hydrogen cyanide, water, benzene with its homologues, naphthalene, carbon disulphide, and tar. For tars an almost linear correlation exists between mean degasification temperature and mean molecular weight. High-temperature tar contains primarily aromatics: phenols, cresol, naphthalenes, benzene and homologues, anthracene. The composition of low-temperature tars varies within a wide range, including paraffins and phenols, also cresols and xylenes, higher phenols and alkylated naphthalenes.

In the classical processing technology of crude gas after the separation of tar and ammonia, crude benzene is obtained in scrubbers. In addition to benzene it contains toluene as well as the three xylene isomers ortho-, meta- and para-xylene. The remaining gas contains about 1.5% ethylene, 0.6% propylene, and 0.2% acetylene. After removal of residual naphthalene, pure coke oven gas is obtained, its main constituents being hydrogen (55%) and methane (24%).

Bituminous coal tar is further broken down by distillation. Technical distillates are light oil, carbolic oil, naphthalene

oil, wash oil, anthracene oil, and pitch, which in their turn are feedstocks for the basic substances of coal chemistry, namely benzene, toluene, xylene, pyridine, aniline, quinoline, phenol and homologues, cresol and naphthalene, anthracene, phenanthrene, etc. The most important of these substances is naphthalene which is produced from naphthalene$_{A}^{oil}$ by multi-stage vacuum distillation. Tar itself still contains 3% naphthalene homologues, especially methyl- and dimethylnaphthalenes, from which, if necessary, additional naphthalene can be produced by thermal and catalytic hydrodealkylation. Similarly, pyridine homologues can be transformed into pyridine by catalytic hydrodealkylation.

Future aspects

If we assume that in the future petroleum and coal will be replaced as energy sources in order to preserve them as secure base of chemical raw materials for many generations to come, then the intermediate products of petrochemical processes most in demand will continue to be small molecules with a relatively high H/C ratio. As has been shown, however, almost all the constituents of natural coal and many constituents of petroleum are substances with high molecular weight and relatively low H/C ratio. Therefore the two major aims of primary chemical processing of coal and higher petroleum fractions are reducing their molecular weights (cracking) and modifying, in most cases increasing, the H/C ratio (hydrogenation). Currently used technological processes such as catalytic cracking, hydrogenation, or hydrocracking achieve these two aims but at present for technological and economic reasons rely largely on feedstocks that are mixtures of substances with medium molecular weight.

The problems to be solved can be illustrated graphically (Figure 6). The characteristic parameters are the atomic H/C ratio

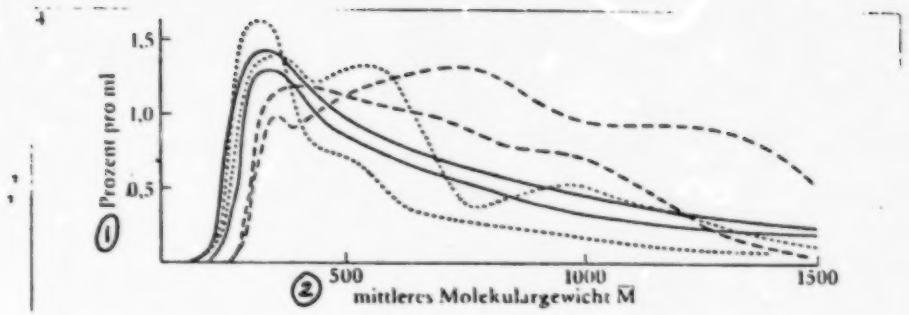


Figure 4. Distribution curves of molecular weights for six German crude oils. The weight percentages of substance in each mL of eluate have been plotted over the molecular weights measured for the individual fractions.
Red solid curve* = Beckendorf crude
Red dashed curve* = Meppen crude
Red dotted curve* = Wahrendorf crude
Black solid curve* = Nienhagen crude
Black dashed curve* = Barenhöf crude
Black dotted curve* = Gernsheim crude

Key: 1 - percent/mL
2 - mean molecular weight

* Please see Translator's note on p. 11.

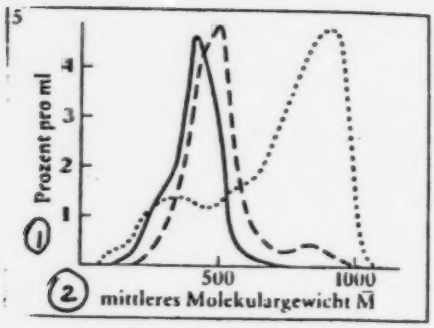


Figure 5. Distribution curves of hydrocarbon, basic and acid fractions of a crude oil in percent of feedstock per eluted volume plotted against molecular weights determined on fractions that were separated gel chromatographically.
Solid curve = hydrocarbon fraction
Dashed curve = basic fraction
Dotted curve = acid fraction

Key: 1 - percent/mL
2 - mean molecular weight

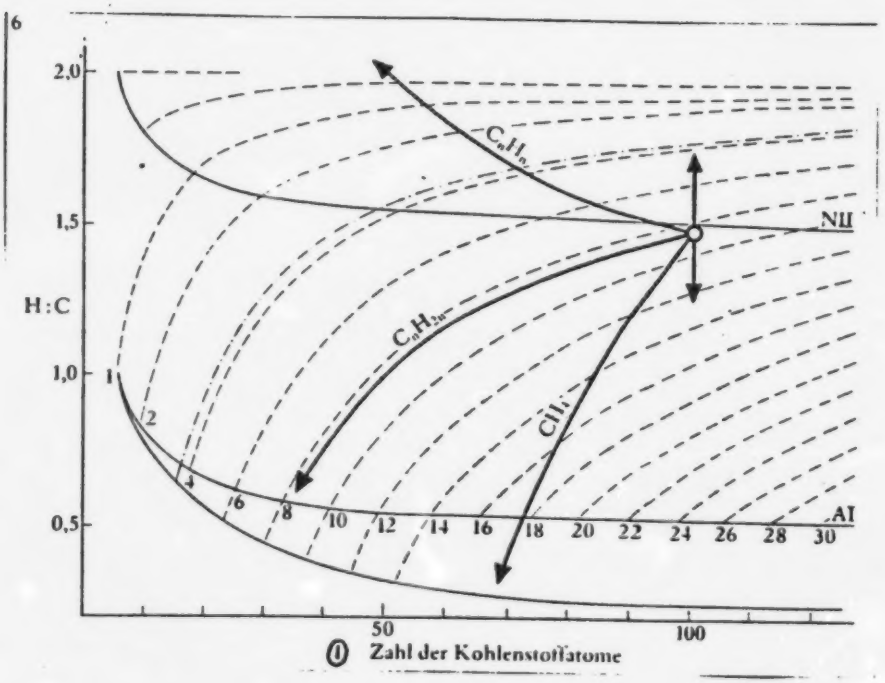


Figure 6. Diagram illustrating conditions during cracking, hydrogenation, and hydrocracking of petroleum distillation residues. The characteristic parameters are the atomic H/C ratio for molecular structure, the carbon number in a molecule of statistically mean properties for molecular size. The figures indicate the number of rings per molecule: 1 = benzene, 2 = naphthalene, 4 = chrysene, etc. The lowest solid line indicates the lower limit of the range of hydrocarbons.

Key: 1 - number of carbon atoms

(ordinate) for molecular structure and the number of carbon atoms in a statistically mean molecule (abscissa) for molecular size. Methane, the smallest hydrocarbon molecule with H/C = 4 and C = 1 would lie to the extreme left and above the indicated range. A polyethylene would be located to the right and outside of the diagram at the level of H/C = 2. If in a large saturated molecule the carbon atoms are not arranged in chains but in condensed rings (e.g. naphthalene), the H/C ratio is less than 2. Such molecules, e.g. perhydrophenanthrene, lie on the line NII. For molecules with the same structure but consisting only of aromatic rings the H/C ratio is considerably smaller; such molecules lie on the line AI. The dashed lines sloping upwards and to the right indicate increasing substitution or substituent size in the ring systems.

To illustrate processing problems, let us assume that a petroleum residue has extreme parameters - 100 carbon atoms (corresponding to a molecular weight of 1350) and a H/C ratio of 1.5. Pure hydrogenation is possible, if at all, only in liquid phase and at high pressures but at moderate temperatures in the presence of active hydrogenation catalysts. Thermodynamically this course would be favoured only at temperatures below 600 K, which makes it kinetically unattractive, for the reaction would be too slow. Without any bond cleavage, the maximum achievable change in H/C ratio would be about + 0.2, and the products of such a reaction would be highly viscous substituted polycyclic naphthenes which would have hardly any uses. As far as process technology is concerned the process used would presumably have to be discontinuous, which would not be attractive. The decisive disadvantage, finally, would be that the heteroatoms of petroleum residues (nitrogen, sulphur, metal) would quickly inactivate any highly active precious-metal hydrogenation catalyst.

Dehydrogenation alone also would result in only a small modification of the H/C ratio and at standard pressure would be thermodynamically and kinetically clearly favoured only at temperatures above 800 K. Under these conditions, however, bond cleavages are already so likely that the carbon atom number of the molecules would not be retained. In the processes used on a technical scale - from visbreaking at 430-480°C and a pressure of several atmospheres to high-temperature coking at 900-1100°C - the formation of gaseous products cannot be prevented. If only methane were being formed the resultant product would follow the CH_4 line in Figure 6. This would reduce the H/C ratio to an undesirable extent while the number of carbon atoms would decrease only moderately; moreover, at rising temperatures appreciable quantities of coke would be generated by dehydrogenating polymerization. It would be more useful, by the judicious selection of process conditions, to hold the empirical composition of the light products being generated at C_nH_{2n} and C_nH_n, usually however at a tendency following the course of line C_nH_{2n}, if coking can be sufficiently suppressed.

Any cleavage aimed at producing hydrogen would follow a hypothetical directrix obliquely upwards and to the left in Figure 6 in the direction towards C = 0 and H/C = ∞ , on the other hand would by necessity, in the sense of a disproportionation, produce a coupling product with C = ∞ and H/C = 0, i.e. coke, which would correspond to a directrix obliquely downwards and to the right.

A course of reaction horizontally to the left, i.e. virtually depolymerization, in purely thermal terms could not be achieved under technical conditions. In the example we have used above this would be prevented by weighty factors. Technically it is not without problems to convert such a high-molecular residue into low-boiling to high-boiling liquid products without the

undesirable coking and at appropriate space velocities. Moreover, the number of heteroatoms (sulphur, nitrogen, metals) increases greatly in high-boiling fractions with low H/C ratios, a fact which on account of environmental pollution would increasingly forbid their use as energy sources (heavy fuel oil).

In the last ten years a technique has thus been developed up to the technical stage which would help remedy this situation: catalytic cracking supported by hydrogenation, or, briefly, hydrocracking. This technique, using pressures of 10-200 bar and temperatures of 200-500°C, cracks high-boiling and non-boiling residues in two process stages. In the first stage nickel (or cobalt) /tungsten (or molybdenum) oxides on aluminium silicates are used as catalysts. Sulphur and nitrogen are converted into hydrogen sulphide or ammonia, respectively, and the residues are cracked into medium distillates. The technical problems at present unsolved are essentially the following: The metal content of the residues greatly impairs catalytic activity so that catalysts can be expected to remain active for periods of up to one year only if the residues have been deasphalted. However, to date no efficient, continuous deasphalting technique has yet been developed that would satisfy all requirements.

Since the molecules used as cracking feedstock are relatively large, an optimum between activity (or specific surface area) and porosity has to be found for the catalyst. Very small pores (to about 30 Å) result in low gross yields and large gaseous fractions. Pores of about 60 Å and above do reduce the specific surface area and thus the activity of the catalyst, but improve molecular transportation, so that high yields of medium distillates are obtained and gaseous fractions are reduced. At temperatures around 500°C, 60-80% of the residues can be converted into medium distillate. Still, at the present state of process technology,

the reaction rate depends too much on the molecular weight of the residues used as feedstock. At optimum adjustment, the rate of cracking a heavy gas oil is still ten times that for non-boiling residues.

In the examples used here, the main product of the first stage is largely free of sulphur and nitrogen, has a carbon number of about 30 and an H/C ratio that is usually unchanged. In a second process stage this product, using mainly precious-metal catalysts and technically established, highly flexible techniques, can be converted for example into high-quality light gasoline for the chemical industry.

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